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MONITORING OF STRUCTURE FORMATION IN THE TECHNOLOGY OF CERAMIC AND SILICATE MATERIALS

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A method is proposed for quantitative assessment of the composition of disperse systems or structures, based on the volume concentration of the component phases for any technological operation in the production of silicate and ceramic materials. The author shows the possibility of using the triple phase diagram and the structure formation criteria, namely, the solid phase volume concentration and the structure-energy parameters, for monitoring and control of structure formation in all the main technological stages.

Any technology related to the use of disperse systems is accompanied by a modification of the quantitative ratio between the individual phases of the disperse system at each stage of the technological process. The most commonly used method for estimating the quantitative relationship between the phases is the weight method (based on the relative weight content of the liquid or solid phase). The unit characteristics are used for the same purpose: true, apparent, and bulk density, and specific volume.

The use of the relative weight and specific parameters does not provide a clear picture of the quantitative content of the gaseous phase, which is an effective structural component in the two-phase (S + G) or three-phase (S + L + G) system.

Therefore, in order to characterize the quantitative composition of a disperse system, it is expedient to use the volume content of the phases which takes into equal account the presence of all phases. In this case, regardless of the type of the technological action upon the system, the following equation is true, which is the mathematical expression of the law of constant volume phase composition of a disperse system:

$$= K_{s_{12}} + K_{l_2} + K_{g_2} = \dots = K_{s_n} + K_{l_n} + K_{g_n} = 1,$$

where K_s , K_l , and K_g are the volume concentrations of the solid, liquid, and gaseous phases in the system at a certain technological stage.

In this case

$$K_s = \rho_s / \rho_m; K_l = W_v = (\rho_s / \rho_l) W_a; K_g = 1 - K_s + K_l,$$

where ρ_s is the apparent density of the material dry layer, kg/m³; ρ_m and ρ_l are the true densities of the material and the liquid, kg/m³; W_v is the volume moisture content of the material, rel. units; W_a is the absolute moisture content of the material, rel. units

In some cases, the volume concentration of the solid phase is used to characterize the relative density of the system or the degree of filling a volume unit with the solid phase, as well as the packing coefficient of the solid phase particles [1, 2].

The use of the volume phase parameters for a disperse system makes it possible to investigate the system's behavior under any technological operation, to elucidate the ratio of the phases during or as a result of a technological action, and to determine the main techniques which can be used to obtain a material with the prescribed structure and properties.

Most production technologies for ceramic and silicate materials involve the need for converting a primary coagulation structure first into a condensation structure and then into a crystallization structure. Such conversion provides for getting maximally dense and strong materials or materials with a prescribed porosity level which have relatively low strength but possess some other valuable properties (porous ceramics, foam glass, claydite).

The formation of the ultimate structure of a material on the basis of a disperse system is accompanied by complex

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physicochemical processes, including chemical and phase transformations. Therefore, one of the main factors for producing materials with maximum homogeneity of structure consists in developing such conditions at the initial stages, which would prevent emergence of defects under any subsequent technological operation.

The development of methods for producing materials with prescribed properties and controlling the processes makes it necessary to model the actual porous systems both at the stage of the system formation and at the ultimate product stage. The most common modeling methods are the physical (or geometrical) method and the mathematical one, which are based on the geometry of regular support particle packing, or on random distribution leading to one of the probabilistic laws of the size distribution of particles.

These models are convenient for characterization of stationary disperse systems, but if a system is a dynamic one which spontaneously evolves in time or under the effect of an external action, the construction of its model requires data on the structural parameters of both the primary structure and the subsequent structures resulting from the effect of various physicochemical factors [7]. This problem can be significantly simplified by using the phase volume system parameters which are closely interrelated with such structural properties as the particle size, shape, and quantity, dispersion and granulometric composition, and the quantity and area of

interparticle contacts per surface unit or volume unit of the system.

L. V. Radushkevich [8], based on the rule of porous media conversion, suggested the following parameter as the comparative porosity criterion:

$$\varepsilon = P/K_s,$$

where P is the porosity; $P = K_g$, which is known in soil science [9] as the porosity coefficient. Let us assume that the initial state of a powder layer or a material with a coherent structure is characterized by the values K_{s_1} and P_1 . If the material is subjected to an action which modifies its initial structural characteristics and its stationary structure is transformed into a dynamic one, the parameters of this new structure can be assessed at any moment using the values K_{s_2} and P_2 . In this case the relative variation of the phase parameter ratios will be

$$\frac{K_{s_2}/P_2}{K_{s_1}/P_1} = \frac{K_{s_2}/K_{s_1}}{P_2/P_1} = \frac{P_1/K_{s_1}}{P_2/K_{s_2}} = n$$

where P is the system porosity, $P = 1 - K_s$; n is a factor indicating the increase or decrease of the relative variation of the solid phase volume content with respect to the relative variation of the volume content of the pores during the transition of the system (or structure) from one state to another in a spontaneous process or under the external energy effect.

It follows from the obtained expression that the informative significance of the porosity coefficient acquires meaning in the evaluation of evolving systems whose structural properties change under the effect of an external action. Taking different initial and ultimate values of the phase parameters of a disperse system, one can determine the regularities and the variation range for the parameter n in compression or expansion of the system. The resulting estimated data can be represented in the form of graphic dependences: $K_{s_2}/P_2 = f(K_{s_1}/P_1)$, $K_{s_2} = f(K_{s_1})$, etc. The estimated values of the parameter n for some states of the system are shown in Table 1.

Analysis of the results represented in Table 1 suggests the following conclusions:

The stationary structures which do not undergo changes under an external action are characterized by the value $n = 1$;

the dynamic structures at $n > 1$ are compressed and at $n < 1$ are expanded under external action;

the systems and structures with a low initial value of K_{s_1} (0.40–0.45) are more sensitive to external action than the structures with a high value of K_{s_1} (≥ 0.7);

the more a system deviates from the stationary state under an external action, the greater is the energy impact exerted on the system.

The value of the parameter n is functionally related not only to the structural and internal energy parameters of the system but also to the external energy action. The level of the

TABLE 1

Initial state of system		Ultimate state of system					
		compression, shrinkage			expansion		
K_{s_1}	P_1	K_{s_2}	P_2	n	K_{s_2}	P_2	n
0.5	0.5	0.5	0.5	1.0	0.5	0.5	1.0
		0.6	0.4	1.5	0.4	0.6	0.666
		0.7	0.3	2.33	0.3	0.7	0.428
		0.8	0.2	4.0	0.2	0.8	0.250
		0.9	0.1	9.0	0.1	0.9	0.111
		0.95	0.05	19.0	0.05	0.95	0.052
0.6	0.4	0.6	0.4	1.0	0.6	0.4	1.0
		0.7	0.3	1.55	0.5	0.5	0.666
		0.8	0.2	2.66	0.4	0.6	0.440
		0.9	0.1	6.0	0.3	0.7	0.255
		0.95	0.05	12.66	0.2	0.8	0.166
		—	—	—	0.1	0.9	0.074
0.7	0.3	0.7	0.3	1.0	0.7	0.3	1.0
		0.8	0.2	1.71	0.6	0.4	0.642
		0.9	0.1	3.85	0.5	0.5	0.425
		0.95	0.05	8.14	0.4	0.6	0.285
		—	—	—	0.3	0.7	0.183
		—	—	—	0.2	0.8	0.107
		—	—	—	0.1	0.9	0.047

energy effect on a system is determined by the type of this action: mechanical action performed to impart the initial shape to the particles, or thermal effect exerted in the removal of moisture from the product by heat drying or removal of a temporary technological binder, and thermal action in firing and sintering of the material. Therefore, the parameter n can justifiably be called the structural-energy parameter of the disperse system and can be used along with K_s as the optimality criterion of structure formation. The difference between the parameters is that K_s makes it possible to assess the degree of accomplishing the goal in structure formation of a system in the stationary state after some external action, and the parameter n allows for quantitative evaluation of both structure formation dynamics and the intensity of the external or internal energy action.

The parameters K_s and n meet all requirements imposed on the optimality or technologic efficiency criteria:

they can be used not just for single operations but for evaluation of the overall technology efficiency;

they have a clear physical meaning and quantitative value;

they are highly sensitive to any disturbances introduced into the systems and have the minimal spread in the disturbance response values;

are universal and take into account both engineering and economic aspects of the technology;

It is expedient to carry out monitoring and analysis of the material structure formation for any operation or for the total process using the parameters K_s and n in the triple coordinate system $K_s - K_l - K_g$.

For example, let us consider a system consisting of Rodionovskii loam and water. The experimental calculation data for this system based on compressive compaction of the mixtures to the water-saturated state (conventional static yield point) are given in Table 2. The specific area of the loam was determined on a PSKh-2 instrument, and the maximum molecular moisture capacity or the least capillary mois-

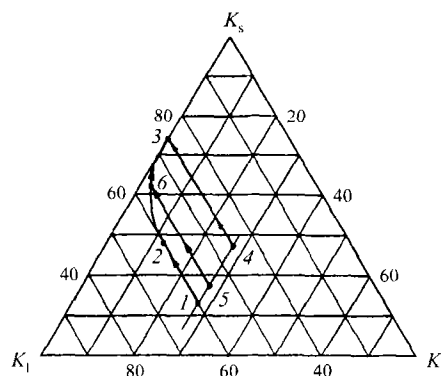


Fig. 1. Variations in the phase volume composition of moist disperse material in compression.

ture W_{icm} , which is a conventional boundary between the capillary-mobile and capillary-immobile moisture, was determined by the Lebedev - Vasiliev method of moisture-consuming media. The thickness of the gas-liquid film (cm) between the particles was calculated by the following equation:

$$d_{il} = \frac{1 - K_s}{K_s} / S_v,$$

where S_v is the specific surface area per solid phase volume unit cm^2/cm^3 ; $S_v = \rho_s S_m$ (S_m is the specific surface area per mass unit, cm^2/g).

The phase composition of the mixture with $W_a = 33.5\%$ in the loose state (Fig. 1) relates to point 1. The consolidation of the mixture under critical pressure results in the modification of the phase composition (point 2, $K_s = 0.480$, $K_l = 0.397$, $K_g = 0.123$, $n = 1.83$). Compression of mixtures with lower initial moisture capacity makes it possible to obtain molded samples whose phase composition is shown in the curve segment 2 - 3. The maximal compaction of the

TABLE 2

$W_{abc}, \%$	Molding pressure, MPa	$\rho_{moist}, \text{kg}/\text{m}^3$	$\rho_s, \text{kg}/\text{m}^3$	K_s	K_l	K_g	$\frac{1-K_s}{K_s}$	$\left(\frac{1-K_s}{K_s}\right)^{1/3}$	$S_v, \text{cm}^2/\text{cm}^3$	$d_{il}, \mu\text{m}$
15.8	16.5	2047	1768	0.716	0.279	0.005	0.396	0.734	4862	0.814
18.1	7.00	2012	1704	0.690	0.308	0.002	0.449	0.765	4686	0.958
19.8	4.60	1976	1650	0.670	0.327	0.003	0.492	0.789	4551	1.081
21.8	3.38	1936	1590	0.644	0.347	0.009	0.552	0.820	4372	1.262
23.6	2.34	1891	1530	0.620	0.361	0.019	0.613	0.849	4207	1.457
25.2	1.70	1845	1474	0.597	0.372	0.031	0.675	0.877	4053	1.665
27.5	1.20	1778	1395	0.565	0.383	0.052	0.770	0.916	3836	2.007
29.7	0.95	1706	1316	0.533	0.391	0.076	0.870	0.954	3619	2.404
31.9	0.71	1658	1257	0.509	0.401	0.090	0.965	0.988	3456	2.792
33.5	0.54	1582	1185	0.480	0.397	0.123	1.080	1.026	3258	3.315

* In all cases $S_m = 2750 \text{ cm}^2/\text{g}$, $r_t = 2470 \text{ kg}/\text{m}^3$.

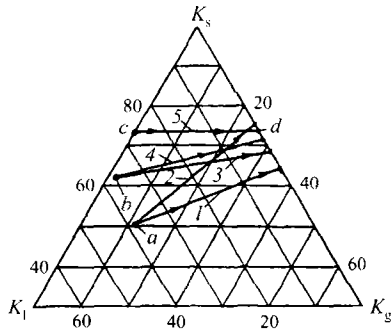


Fig. 2. Variations in the phase volume composition of moist disperse material in drying: a) mixture 6; b) mixture 1; c) Rodionovskii loam with $W_{icm} = 14.2\%$; 1) mixture 6, $t_s = 150^\circ\text{C}$; 2) mixture 6, $t_s = 20^\circ\text{C}$; 3) mixture 1, $t_s = 150^\circ\text{C}$; 4) mixture 1, $t_s = 20^\circ\text{C}$; 5) Rodionovskii loam with $W_{icm} = 14.2\%$, $K_l = 0.26$, $t_s = 150^\circ\text{C}$.

moist material is attained at point 3 with $W_{icm} = 14.2\%$ ($K_s = 0.74$, $K_l = 0.26$, $K_g = 0$). The transition of the mixture with $W_{icm} = 14.2\%$ from the loose state (point 4) to the two-phase state (point 3) corresponds to line 4–3 at $n = 3.14$. This value of the parameter n indicates that a rather substantial external energy action ought to be exerted on the system in order to reach its maximum density.

When a mixture with the optimum molding moisture $W_a = 22.6\%$ is condensed, its initial phase composition (point 5) is located on line 1–4 at $K_{s_2} = 0.355$, and after condensation under the critical pressure (point 6) it is on curve 2–3 at $K_{s_2} = 0.63$, $K_{l_2} = 0.352$, and $K_{g_2} = 0.018$. With this ratio between the phases, the restructuring of the mixture is much less significant ($n = 2.45$). The process of clay slip ($K_{s_1} = 0.3$, $K_{l_1} = 0.7$) dehydration in a gypsum mold proceeds along the line $K_s - K_l$ up to $K_{s_2} = 0.74$, i.e., to $W_{icm} = 14.2\%$ and $K_{l_2} = 0.26$. This method of dehydration and condensation relates to the parameter $n = 6.64$, i.e., dehydration of the material through the capillary forces is characterized by a higher level of energy action and restructuring.

As the moist material dries, the coagulation structure is converted to a condensation structure, and the parameter n can be used as well to estimate the volume variations of the material upon moisture removal. This assumption was verified on mixtures 1, 2, and 3 prepared from Rodionovskii loam with varying initial moisture content and mixtures 4, 5,

and 6 made from the same loam with additives of 10, 20, and 30% bentonite, respectively. The samples were shaped as $2.5 \times 2.5 \times (2 - 2.5)$ cm cubes (the mold) and dried at temperatures 20, 50, 100, and 150°C . Before and after drying, the size and weight of the samples were measured and all necessary parameters were calculated on this basis. At the same time, the drying sensitivity coefficient of the mixture K_{sens} was calculated according to Z. A. Nosova. The experimental results are shown in Table 3, and their analysis suggests the following conclusions:

the maximum volume variations in the material are observed at the drying temperature $t_d = 20^\circ\text{C}$;

an increase in the drying temperature decreases the volume variations, which can be inferred from K_{s_2} and n ;

introduction of bentonite additives to the mixture composition significantly intensifies the volume variations in the material in the course of drying due to the decreased solid phase content and increased volume content of moisture in the initial state;

an additive of bentonite contributes to an increase in the gaseous phase content in the material;

an additive of bentonite (up to 10%) improves the coherence of the moist material due to increased forces of adhesive-cohesive interaction between the structural skeleton particles and the pore material; as the bentonite content increases, the equilibrium of these forces is disturbed owing to increased volume variations, and the drying sensitivity of the mixtures increases.

Analysis of Nosova's formula for calculation of K_{sens} ,

$$K_{sens} = V_s / V_{por},$$

and the volume changes in drying of a moist material shows that the relative shrinkage of the material can be determined from the difference

$$V_s = K_{s_2} - K_{s_1},$$

and the volume of pores in the dry material as

$$V_{por} = 1 - K_{s_2}.$$

Consequently,

$$K'_{sens} = ((K_{s_2} - (K_{s_1})) / (1 - (K_{s_2}))).$$

TABLE 3

Mix- ture	W_f , rel. units	P_f , MPa	ρ_{moist} , kg/m ³	ρ_s , kg/m ³	K_{s_1}	K_{l_1}	K_{sens}	$t_s = 20^\circ\text{C}$			$t_s = 50^\circ\text{C}$			$t_s = 100^\circ\text{C}$			$t_s = 150^\circ\text{C}$			m_{3v}
								K_{s_2}	n	K'_{sens}	K_{s_2}	n	K'_{sens}	K_{s_2}	n	K'_{sens}	K_{s_2}	n	K'_{sens}	
1	0.226	0.51	1908	1556	0.630	0.352	—	0.710	1.44	0.27	0.700	1.37	0.23	0.696	1.34	0.22	0.688	1.29	0.18	1.59
2	0.198	1.53	1968	1642	0.665	0.325	1.70	0.747	1.48	0.32	0.746	1.48	0.32	0.736	1.40	0.27	0.730	1.36	0.24	1.50
3	0.185	2.05	1990	1679	0.680	0.311	—	0.759	1.48	0.32	0.752	1.42	0.29	0.751	1.42	0.28	0.748	1.39	0.27	1.47
4	0.216	2.25	1767	1453	0.590	0.314	1.96	0.765	2.26	0.74	0.763	2.23	0.73	0.762	2.22	0.72	0.760	2.20	0.71	1.69
5	0.255	2.56	1668	1329	0.543	0.339	2.37	0.764	2.72	0.94	0.762	2.69	0.92	0.738	2.37	0.74	0.730	2.27	0.69	1.84
6	0.324	2.05	1618	1222	0.501	0.396	2.54	0.747	2.95	0.97	0.741	2.86	0.93	0.651	1.86	0.43	0.645	1.82	0.41	2.00

It is seen in Table 3 that in spite of the significant differences between the numerical values of K_{sens} and K'_{sens} , both coefficients adequately reflect the drying sensitivity of the material and react similarly to the volume variations of materials in drying. The following linear dependence is observed between the parameters K'_{sens} and n :

$$n = mK'_{\text{sens}} + 1,$$

where m is the proportionality coefficient.

The value of the coefficient m_{av} (Table 3) virtually does not depend on the drying temperature and is only determined by the mixture moisture and composition. The dependences $n = f(K'_{\text{sens}})$ for various mixtures is a pencil of straight lines starting from the point with the coordinates $(n = 1, K'_{\text{sens}} = 0)$ and having different values of slope m_{av} , which can be used as well to estimate the drying sensitivity of the materials.

As distinct from m_{av} , the parameter n reacts to the drying temperature as well and decreases with an increase in t_d due to the formation of a less moist and more rigid shell on the material surface, which impedes volume shrinkage of the material. It can be seen in Table 3 that regardless of the drying temperature of the material, the sum of the relative values of drying shrinkage volume of the material and the porosity volume after drying is a constant value

$$\begin{aligned} V_{\text{por}} + V_s &= (1 - K_{s_2}) + (K_{s_2} - K_{s_1}) \\ &= 1 - K_{s_1} = K_{l_1} + K_{g_1}, \end{aligned}$$

and is equal to the overall volume content of the liquid and gas phases in the initial material before drying. The obtained relationship reflects the phase volume equilibrium of the material in drying and is a particular case of the law of constant volume phase composition of a disperse system. Based on this law, the drying process can be also represented on the phase diagram $K_s - K_l - K_g$ (Fig. 2). The variation of the phase composition of the samples in drying relates to the straight line which connects the initial and the ultimate phase composition of the material after drying shown on the line $K_s - K_g$.

The analysis of the behavior of mixture in drying gives reason for additional deductions:

removal of moisture in drying increases the volume concentration of the solid phase (K_{s_2}) regardless of the drying temperature;

with lower initial moisture of the material, a higher value of K_{s_2} is attained;

an increase in drying intensity results in a decrease in K_{s_2} ;

the more drying-sensitive materials exhibit higher values of the difference $K_{s_2} - K_{s_1}$ and the parameter n under the same drying conditions;

an increase in the gas phase content in the initial mixture increases the mixture drying sensitivity.

The most compact structure of the material based on Rodionovskii loam can be obtained after drying the mixture

with the moisture content $W_f = W_{\text{icm}} = 0.142$ ($K_{l_1} = 0.26$). In this state ($K_{s_1} + K_{l_1} = 1$) the mixture has the highest degree of coherence and mechanical strength due to the minimum thickness of the liquid interlayer ($d_{ll} = 0.7 \mu\text{m}$) between the particles. This moisture is removed in drying in the form of steam and its removal is not accompanied by shrinkage ($K_{s_1} = K_{s_2} = 0.74$, $n = 1$), and the variation in the material phase composition in drying relates to the line $c - d$ in Fig. 2.

The sintering of material in firing is the process of conversion of a condensation structure to a more ordered and stronger structure, i.e., the crystallization structure, and this process is shown in the phase diagram along the line $K_s - K_g$ within the limits of $0 < K \leq 1$. The possibility of using the parameters K_s and n in sintering is demonstrated in [10].

The law of constant phases and the phase diagram can be used to analyze processes which take place in the production of porous materials, including foam glass, foam silicates based on liquid glass, light-weight refractories and porous ceramics, claydite, gas concrete, and other materials.

The above described example of using the phase diagram and the parameters K_s and n reveals the possibility of using this method in analyzing the formation of structures based on any disperse systems used in ceramic and silicate technologies. The proposed method makes it possible to quantitatively estimate the efficiency of various additives and techniques in molding, drying, and firing of materials and can be used in modeling disperse structures and technological operations.

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